

EXHIBIT 3

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(71) Applicant (*for all designated States except US*): **EID-
GENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH** [CH/CH]; Rämistrasse 101, CH-8092 Zürich
(CH).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **STARK, Jan,
Wendelin** [CH/CH]; Mockentobel 3, CH-8400 Winterthur
(CH). **PRATSINIS, Sotiris, E.** [US/CH]; Aurorastrasse
73, CH-8032 Zürich (CH).

(74) Agent: **E. BLUM & CO.**; Vorderberg 11, CH-8044 Zürich
(CH).

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(54) Title: METAL DELIVERY SYSTEM FOR NANOPARTICLE MANUFACTURE

(57) Abstract: Abstract: Described is a method for the production of pure or mixed metal oxides, wherein at least one metal precursor that is a metal carboxylate with a mean carbon value per carboxylate group of at least 3, e.g. the 2-ethyl hexanoic acid salt, is formed into droplets and e.g. flame oxidized. The method is performed at viscosities prior to droplet formation of usually less than 40 mPa s, obtained by heating and/or addition of one or more low viscosity solvents with adequately high enthalpy.

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METAL DELIVERY SYSTEM FOR NANOPARTICLE MANUFACTURE

Technical Field

The present invention concerns a specific
5 type of manufacturing method for metal oxides and metal
oxides with specific features that are obtainable by said
method, in particular cerium, zirconium, gadolinium,
iron, manganese oxides, mixed oxides, in particular earth
alkaline titanates, alkali manganates, stabilized
10 zirconia and ceria.

Background Art

Metal oxides, in particular mixed metal
oxides have a broad range of applications such as e.g.
15 ceramics, polymer additives, fillers, pigments, reactive
surfaces, catalysts, storage materials, polishing
additives, membranes, fuel cells etc. Among the most
important metal oxides are cerium oxide, cerium-zirconium
and other stabilized zirconia mixed oxides, titanates and
20 other mixed oxides below referred to as ceramic oxides.
If these materials are used as nanoparticles (particle
diameter below 200 nm), they exhibit advantageous
properties such as high catalytic activity, improved
processing capability, low sintering temperature, good
25 dispersion capability, just to name a few. Titanates are
used as dielectrics for capacitors. Nanoparticles are of
high interest as reduced feature size requires thinner
sheets of dielectrics and since such thinner sheets are
preferable made from very small particles, for example,
30 nanoparticles.

Current methods for the production of metal
oxides are mechanical and mechanical/thermal processes,
wet-phase chemistry based methods, and high temperature
methods such as flame spray pyrolysis (FSP). For the
35 latter, energy to drive the conversion to nanosized
oxides can be radiofrequency (plasma), microwaves, laser
or shock waves. Most convenient, however, is the use of

thermal energy since in most cases this is the least expensive source of energy.

Mechanical and mechanical/thermal methods are energy intensive (milling!) and generally suffer from
5 insufficient mixing at the atomic level leading to low phase stability and/or low specific surface area. Impurity from the milling (abrasion) reduces product purity and performance.

Wet-phase based methods entail huge solvent
10 costs, produce large amounts of waste water and need calcination steps after the synthesis, making them cost intensive. Furthermore, although e.g co-precipitation of ceria/zirconia can lead to mixed oxide powders with extremely high specific surface areas, unfortunately, the
15 temperature stability of as-prepared oxides is characterized by a big loss of specific surface area at elevated temperature. The same observation applies for most wet-phase made ceramics. Preparation at high temperature may produce an oxide with increased
20 stability. This has prompted several people to attempt to prepare oxides by flame spray based methods. Flame spray pyrolysis (FSP) is a known process and has been used for preparation of many oxides. It uses thermal energy and has the inherent advantage of supplying low cost energy
25 to drive nanoparticle formation. However, in the case of many oxides, the research for suitable precursors entails huge problems associated with the chemical properties of these compounds. For example Yoshioka et al. (1992) used FSP for the production of ceria oxides, but they received
30 a powder of low specific surface area. WO 01/36332 discloses a FSP method leading to an inhomogeneous product comprising ceria particles of broadly varying sizes. Aruna et al. (1998) investigated the ceria/zirconia synthesis by combusting mixtures of redox
35 compounds and oxidizing metal precursors. This high temperature preparation yielded a high surface area product with apparently good phase mixing in as-prepared

powders. However, the preparation of ceramics by solid combustion is difficult to realize at high production rates, since the process may quickly run out of control. Furthermore it is basically a batch process and the reproducibility is a general problem. Laine et al. (1999) and Laine et al. (2000) used a spray pyrolysis unit to prepare ceramic oxides but the specific surface area of the product powder stayed low, at 10 to 16 m²/g. EP 1 142 830 also discloses a FSP method for the preparation of ceria/zirconia starting from organometallic compounds in organic solvents and/or water. The procedure disclosed in EP 1 142 830 focuses on chlorine free powders produced by flame spray pyrolysis and uses precursor solutions of type MeR where R is an organic rest such as methyl, ethyl, or a corresponding alkoxy-rest or a nitrate anion. As solvents, water or alcohols are used. US 5'997'956 discloses a procedure where a liquid or liquid like fluid near its supercritical temperature is injected in a flame or plasma torch and thereby converted to nanoparticles.

WO 02/061163 A2 discloses an apparatus for the production of powders or film coatings. Thereby, the metal containing liquid is atomized without the use of a dispersion gas. Oljaca et al. (2002) describe a process using similar nozzles for the manufacture of nanoparticles. They only describe very low production rates with solutions being less than 0.05 M in metal. Droplet size distribution is stated as a major parameter for the successful nanoparticle synthesis. They report on the synthesis of yttria stabilized zirconia amongst others.

Recently Mädler et al. (2002B) disclosed an FSP method for the production of pure ceria with high surface and homogeneous particle sizes using a two phase nozzle to disperse the metal containing liquid by a dispersion gas (oxygen or air) and igniting the resulting spray by a premixed flame surrounding said nozzle. Such burner is furtheron in this document termed a spray

burner. The solvent system used by Mädler et al., however, has now been found to be unsuitable for the production of e.g. ceria/zirconia. Stark et al. (2003) disclose the use of acetic acid and lauric acid for the preparation of ceria, zirconia and ceria/zirconia. Maric et al. (2003) use a not further specified $C_xH_{2z}CeO_6$ precursor for the preparation of ceria, gadolinia and samaria doped ceria for fuel cell membranes. They applied a dispersion gas free atomization device working at low production rate and using a Nanomiser device (WO 02/061163 A2, see above) that makes very small droplets (below 10 micrometer). Overall production rate even using such a multiple nozzle setup is still below 1 kg/h.

In order to bring the nanoparticle manufacture from the pilot-scale production to an industrial scale synthesis (kg to ton quantities), some additional problems are to be faced. The most prominent is the choice of readily accessible metal precursors that allow sufficiently high production rates. The present invention links the manufacture of nanoparticles to existing metal containing products that were developed for different applications but not the manufacturing of nanoparticles. A second problem is production rate. Using multiple arrays as in WO 02/061163 A2 entails problems with maintenance, nozzle clogging, space, reproducibility and others. It would be much preferred to use few burners to make the same quantity of powder. It would further be of much use to apply a metal carrier liquid that can be sprayed on most conventional oil burners and does not require the sophisticated atomisation devices as e.g. in WO 02/061163. This further much helps scaling the production further up as oil burners with well above 100 kg oil/h are available. As it will become apparent within this invention, such a burner could achieve up to 20 kg ceramic particles per h (for 100 kg feed/hour).

For e.g. ceria, zirconia and ceria/zirconia all hitherto known methods use dilute metal solutions

(usually <0.15 moles of metal/liter) resulting in low production rates. High metal concentrations are favorable as they directly increase the production rate of the process. Therefore, the metal concentration in the carrier liquid should be as high as possible. In the scope of the present invention, the flame spray process was found to limit the range of possible carrier liquid formulations by the viscosity as the liquid has to be dispersed during the process. While droplet size was found to be of minor importance, very viscous liquids could not be sprayed at all. It is therefore of high interest to find precursors for flame spray synthesis of oxide and metal nanoparticles that combine low viscosity and high metal concentration. Furthermore, such formulations should be readily produced and be stable upon storage. It is yet another objective of the present invention to show that common oil burners can be used for the synthesis of nanoparticles if the metal carrier liquid exhibits the above mentioned characteristics.

20

Disclosure of Invention

Hence, it is a general object of the invention to provide a method suitable for the production of metal oxides with improved features and therefore extended applications as well as such metal oxides.

Another object of the present invention is a ceria, zirconia, stabilized zirconia, iron or manganese oxide, lithium manganate or calcium- and barium- titanate nanopowder with high homogeneity and produced at high production rate.

Still other objects of the present invention are the use of a metal oxide of the present invention as at least part of a catalytically active system, in particular for combustion engines, or for mechanochemical polishing, or in magnets, in electronic components,

mechanical actuators, as piezoelectric or energy storage elements.

It is yet another objective of the present invention to stabilize zirconia by adding another metal
5 oxide such as ceria, gadolinia or yttria for applications in fuel cells, sensors and as structural ceramic or for coatings.

It is again another objective to show that common oil burners can be used for the synthesis of
10 nanoparticles if metal containing liquids of specific quality are applied.

It is another objective that technical metal formulations are well suited for nanoparticle synthesis. While impurities are reducing the thermal stability, such
15 particles may still be of high interest for high-volume applications where purity is of minor importance. Such applications may be as opacifiers in ceramics (low grade zirconia).

Now, in order to implement these and still
20 further objects of the invention, which will become more readily apparent as the description proceeds, the metal oxides of the present invention are manifested by the features that they are obtainable by the method of the present invention.

25 The method for the production of a metal oxide of the present invention, is characterized in that at least one metal carboxylate (the salt of a metal with a carboxylic acid) is dissolved in a high enthalpy (usually > 25 kJ/g) solvent comprising up to at most 40 %
30 of a carboxylic acid or a carboxylic acid mixture to form a solution, and wherein said solution is then formed into droplets and converted to nanoparticle by means of a high temperature process. Such metal carboxylates, also known as metal soaps, are generally used in large quantity as
35 siccatives in resins, lacquers, as additives in polymer manufacturing, as fuel additives and in the fabrication of thin films. Some also find use as metal source for

animal skin preservation. Therefore, such metal soaps are readily available, stable and readily processed, or they can be obtained by treating metal precursors with a suitable acid, optionally and often preferably at higher
5 temperature. Suitable metal precursors are those with anions that are easily replaced. Preferred anions are those that in protonated form are easily removable, such that no equilibrium can establish and the reaction proceeds to almost 100%, e.g. oxides, hydroxides,
10 carbonates, halides, such as chlorides and bromides, and lower alkoxides.

Either pure (many of these metal soaps have a low melting point such that at enhanced temperature they have a sufficiently low viscosity) or dissolved in an
15 additional solvent, such metal soaps are a highly suitable precursor for the manufacture of nanoparticles. Part of their most advantageous use is the fact that very high production rates can be used (in dissolved form, more than 100 g of ceria per liter of carrier liquid, or
20 over 200 g zirconia per liter carrier liquid) which becomes a major problem in conventional preparation methods. There, solubility of the metal or high viscosity (difficult to spray) limit the production rates to low values (Mädler et al., 2002 achieved 26 g ceria per liter
25 of precursor liquid). Oljaca et al. (2002) used less than 0.05 M solutions (corresponds to 8.6 g ceria or 6 g zirconia/h) while according to the invention above 1 M solutions can be made.

It has been found that using a precursor mix
30 as disclosed in the scope of the present invention in FSP allows the production of pure and mixed oxides such as ceria, zirconia, gadolinia, titanates, manganates and stabilized zirconia at high production rate while preserving the beneficial properties of good mixing at
35 atomic level, excellent specific surface area (e.g. good accessibility) and high phase stability.

A precursor or precursor mix, respectively, for FSP needs to carry sufficient metal(s) into a high temperature zone or preferably the flame, distribute said metal(s) within the high temperature zone or the flame and support a stable combustion or conversion and spray process. In the case of many metals such as for example cerium, this entails the following problems:

- Few organometallic compounds are known, all organometallic compounds are rather expensive and/or contain other, undesired elements such as halogenes.

- Cheap precursors are mainly water soluble. Water, however, is a very bad basis for FSP since it is cost and equipment intensive to achieve the necessary high temperature (plasma, laser, microwaves, high dilutions).

The here disclosed process avoids these limitations.

Brief Description of the Drawings

The invention will be better understood and objects other than those set forth above will become apparent when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings, wherein:

Figure 1 shows a conventional oil burner (dispersion nozzle) with guiding tube removed top view. The middle consists of a 2-phase nozzle where the oil or, in this case, metal containing liquid is dispersed. The sectioned channel delivers air to support the combustion.

Figure 2 shows a conventional oil burner producing calcia stabilized zirconia nanoparticles at 540 g/h.

Figure 3 shows transmission electron microscopy images of ceria/zirconia (CeZrO_4) prepared

from a 0.4 M solution of Ce and Zr (each 0.4 M). On the left is a transmission electron microscope (TEM) picture of ceria/zirconia $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ as prepared by using a production rate of 118 g/l of carrier liquid. On the right is a transmission electron microscope (TEM) picture of ceria/zirconia $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ after thermal treatment at 700°C, 16 h, air, showing that such thermal treatment leads to larger particles of similar shape.

Figure 4 shows an X-ray diffraction spectrum (XRD) diagram of CeZrO_4 prepared from 0.4 M solutions of Ce and Zr.

Figure 5 shows the X-ray diffraction spectrum (XRD) of gadolinia doped ceria ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$; gadolinia/ceria) as prepared. It depicts the broad signals of very small crystals and confirms the excellent degree of mixing of the two metals and - by the clear peaks - it underlines the phase stability of the mixed oxide. It shows how different oxides can be delivered in the flame extremely homogeneously as to form a pure mixed oxide phase.

Figure 6 depicts the XRD diagram of manganese oxide nanoparticles prepared from manganese naphthenate.

Figure 7 is a XRD diagram of BaTiO_3 prepared from barium and titanium precursors, dissolved in 2-ethylhexanoic acid, and with xylene as solvent. It confirms the identity of barium titanate nanoparticles by XRD.

Figure 8 is a XRD diagram of calcium titanate from calcium octoate and titanium octoate prepared from titanium tetra isopropoxide and 2-ethylhexanoic acid showing that calcium titanate can be obtained from calcium and titanium containing precursors that are converted into metal soaps. The low curve gives the XRD as prepared and the top gives the oxide after a sintering at 600 °C, 2h in air. A TEM image of the product is shown in Figure 9.

Figure 9 gives TEM images of electronic materials prepared as in the experimental procedure. Left: LiMn_2O_4 particles for usage in battery storage materials, right: CaTiO_3 for usage as dielectric or in other applications. In both materials, rather uniform particle size is observed, indicating a homogeneous particle formation throughout the reactor.

Figure 10. is the XRD diagram of gadolinium oxide prepared from the corresponding gadolinium octoate in xylene/2-ethylhexanoic acid (10:1 by volume).

Figure 11 gives the XRD diagram of lithium manganese oxide. The as prepared powder mainly consists of hausmannite and some amorphous parts. Heating to 400 °C is sufficient for the formation of the mixed oxide spinell phase.

Modes for Carrying out the Invention

The metal oxides of the present invention are obtainable by a method wherein at least one metal carboxylate ("metal soap") is used pure or dissolved and wherein said liquid is then formed into droplets and oxidized in a high temperature environment, in particular a flame.

The current invention uses metal carboxylates (salts of metals with one or several carboxylic acids) as a metal source for high temperature conversion to nanoparticle oxides, in particular flame spray synthesis. The metal soaps are used pure or dissolved in an additional solvent as to achieve a suitable viscosity.

In a much preferred embodiment of the inventive method the precursor liquid essentially consists of one or several metal soaps (presence of usual impurities of technical solvents is acceptable) pure or dissolved in a solvent. Optionally, these precursors may be heated prior to spraying. The liquids are characterized by a net heat of combustion of at least 13

kJ/g for some metals, preferably, and more generally applicable at least 18 kJ/g, more preferably at least 22.5 kJ/g, most preferably at least 25.5 kJ/g, and a viscosity of less than 100 mPas, preferably less than 50 mPas, most preferably less than 20 mPas. This is achieved by using pure metal soaps (optionally heated to elevated temperature that reduces their viscosity) or by dissolving metal soaps in an additional solvent with suitable viscosity and combustion energy.

10 In order to reduce the viscosity of the precursors it is often favorable to use a mix of a hydrocarbon such as toluene, xylene, hexane or light paraffin oil and a metal carboxylate where the corresponding carboxylic acids have a mean carbon number
15 of at least 3 per carboxylate group as to ensure low viscosity, sufficient solubility and combustion energy. Preferred solvent mixes comprise metal soaps with a mean carbon number per carboxylate group of at least 4, more preferred of at least 5, in particular 5 to 8, whereby
20 the carboxylic acid usually has not more than 30C and preferably is selected from one or more C3 to C18 monocarboxylic acids, more preferred from one or more C4 to C12 carboxylic acids, and most preferred from one or more C5 to C8 carboxylic acids. Even though a higher mean
25 carbon content than 8 can be used, such higher mean carbon content usually reduces the production rate.

Also suitable are chelating acids, such as dicarboxylic acids, polycarboxylic acids, amino carboxylic acids, hydroxy carboxylic acids, provided that
30 they provide sufficient enthalpy or are compatible with the solvent optionally present to lower the viscosity and/or to enhance the enthalpy. Suitable carboxylic acids comprise linear or branched chain acids that can be saturated or unsaturated, and optionally further
35 substituted as long as the substituents do not unduly affect the high enthalpy of the acid that preferably is at least 13 kJ/g, more preferably at least 18 kJ/g, much

preferably at least 22.5 kJ/g and most preferably at least 25.5 kJ/g, or the melting point or the solubility of the metal soap. For many heavy metal oxides, metal soaps of 2-ethylhexanoic acid exhibit the desired
5 properties and are well suited for flame spray synthesis. In other cases, such as the production of titanates, the metal soaps can be directly made in situ from a metal containing precursor by reaction with a carboxylic acid. Such solutions can be mixed with another metal soap and
10 readily produce metal oxides, e.g. titanates such as calcium- and barium titanate. As already mentioned above, suitable metal precursors are in particular those with an anion that in protonated form can easily be removed, e.g. by heating, optionally under vacuum.

15 Beyond metal soaps with unsubstituted monocarboxylic acids, as already addressed above, other metal carboxylic acid salts can be applied as far as some limitations are observed. In this case it may be advantageous or even necessary to add an acid to the
20 solvent in an amount of usually at most 40 %. Dependent of the one or more acids derived anions of the metal soap, the one or more acid used as solvent can be linear or branched, saturated or unsaturated, unsubstituted or substituted monocarboxylic acids provided that they
25 result in a suitable high enthalpy solvent. Such acids comprise acids with polar substituents such as -OH, -NH₂ or -CONH₂ groups that can be used to adjust the solvent to specific needs. In specific cases also sufficiently long chain optionally substituted saturated or
30 unsaturated dicarboxylic acids or polycarboxylic acids can be used.

 In many cases, however, no acid is needed or even disadvantageous. It has been found that metal carboxylates with higher mean carbon content, in
35 particular salts with at least C₄ monocarboxylic acids, preferably at least C₅ monocarboxylic acids, are readily dissolved in apolar solvents with low molecular weight

and/or low viscosity such as toluene, xylene, lower alkanes such as hexane, white spirits, but also light paraffin oil, ethers etc.

Presently preferred metal soaps are those
5 with unsubstituted, linear or branched, saturated or unsaturated monocarboxylic acids, in particular C5 to C8 monocarboxylic acids such as e.g. 2-ethyl hexanoic acid, and preferred solvents are at least 60 %, preferably at least 80 %, much preferred almost 100 % apolar solvents,
10 in particular solvents selected from the group comprising toluene, xylene, lower or low viscosity alkanes, such as hexane, isooctane, lower or low viscosity alkenes, lower or low viscosity alkynes, or mixtures thereof.

In yet another manifestation of the present
15 invention, an oxide can be converted into nanoparticles by in situ forming the metal soap by treating the precursor, e.g. the oxide, hydroxide, halide, carbonate or alkoxide, at elevated temperature with the corresponding one or more carboxylic acids , eventually
20 reducing viscosity by adding an additional solvent and oxidizing, in particular flame spraying the resulting mixture. The resulting oxide is made of nanoparticles of very narrow size distribution. Scheme 1 below outlines the procedure.

Scheme 1. The carboxy process for the conversion of an oxide into corresponding nanoparticles.

5

Procedure	Example
Oxide	Gadolinium oxide (99 %)
Make metallic soap	66.6 g Gd ₂ O ₃ , 200 ml of 2-Ethylhexanoic acid, 35 ml acetic acid anhydride, reflux at 140 °C for 10 h, some acetic acid removed
Adjust viscosity	Dilute metal soap with xylene
Flame spray	Spray in a methane/oxygen flame as reported in the Experimental section
Collect nanoparticles	Gd ₂ O ₃ nanoparticles with 70 m ² /g surface area.

In the inventive method, the flame or high temperature zone has a temperature of at least 600°C, usually at least 1200°C, preferably at least about 1600°C. A preferred range of the flame temperature for many applications is 1200 to 2600°C.

The average diameter of the droplets can vary depending on the liquid dispersion setup and the properties of the liquid itself. Usually, the average droplet diameter ranges from 0.1 µm to 100 µm, preferably from 1 µm to 20 µm. The droplet diameter is of minor importance if a here described precursor solution is applied. This is very advantageous as it allows for most conventional, commercially available oil-burners to convert the here described liquid into corresponding oxides. Suitable oil-burners are - to only mention a few

- available from Vescal AG, Heizsysteme, Industriestrasse 461, CH-4703 Kestenholz under the designation of OEN-151LEV, or OEN-143LEV, or OEN-331LZ to OEN-334LZ.

Preferably, the droplets subjected to heat
5 oxidation comprise the metal in concentrations of at least 0.15 moles metal per liter. Such concentrations lead to production rates of at least 0.15 moles metal or metal oxide per nozzle.

If the method of this invention is performed
10 using a flame with insufficient oxygen for full conversion, such oxygen deficiency results in the formation of substoichiometric oxides or metals and mixtures thereof that have also their applications.

Furthermore, by adding a further step after
15 the oxidation, the as produced metal oxides can be converted to the corresponding non-oxides such as nitrides, borides, carbides by means of an additional treatment, such as a treatment with ammonia, hydrogen, etc.

20 The method of the present invention can be used for the production of a broad range of metal oxides, in particular also mixed metal oxides. Further oxide systems that may be prepared by the inventive method, using specific carboxylic acids as solvent are e.g. pure
25 transition metal oxides and mixed alkali or alkaline earth metal and transition metal oxides such as alkali metal manganates, especially lithium manganate or cobaltates, or calcium, strontium, barium titanates or zirconates and mixtures thereof, but also other oxides
30 such as iron or manganese oxides.

Such oxides, in particular if prepared from pure precursors, have a high thermal stability that is characterized by a specific surface area (BET) of at least 20 m²/g after sintering for 1 h at 600°C.

35 In contrast to impurity free pure or mixed metal oxides, oxides with impurities and superior features than hitherto known can be produced that usually have a

specific surface area (BET) of at least 5 m²/g after high temperature oxidation, preferably at least 10 m²/g, in particular at least 15 m²/g. Impurities allowing such surface areas are e.g. alkali metals, earth alkali

5 metals, transition metals or rare earth metals, but also chlorides, fluorides or bromides, phosphates, sulfates or silicon and main group metals, such as Al, B etc., in the range of 0.5 to 5 % per weight, in particular from 0.8 to 5 % per weight.

10 A preferred metal oxide obtainable by the method of the present invention is characterized by a geometric standard deviation of the mass averaged primary particle size distribution smaller than 2 or with less than 2 wt% of solid primary particles with more than 500
15 nm in diameter and a specific surface area of more than 3 m²/g. Such metal oxide particles are suitable for powder injection molding or optical lens polishing.

Much preferred metal oxides are zirconia stabilized with cerium and/or yttrium, preferably cerium
20 or yttrium, in particular in an amount of cerium and/or yttrium of at most 20 %.

Ceria based oxides in general and zirconia based oxides in general, but also LiNbO₃, BaTiO₃, SrTiO₃, CaTiO₃, Li_yMnO_x and derivatives, NiO, Li_xTiO_y, apatite for
25 medical implants, metal doped titania, rare earth metal oxides, especially lanthanum based perovskites, mixed oxides containing an element of the earth metal and from the transition metal group, mixed oxides containing an element from the alkali metals and the transition metals,
30 aluminates, borates, silicates, phosphates, hafnia, thoria, uranium oxide, etc. with specific properties are obtainable. A series of representative examples is given in the experimental section.

The method of the present invention also
35 encompasses the production of metal oxides starting from metal soaps that are combined with other precursors, in particular organometallic or organometalloide precursors,

provided that the solubility and enthalpy stay within the herein outlined ranges. The as-prepared oxides may be subjected directly to an after-treatment in order to form nitrides, carbides, silicides, borides and others.

5 Suitable metals for the production of pure or mixed metal oxides are e.g cerium, zirconium, any rare earth metals, lithium, sodium, potassium, rubidium or caesium, magnesium, calcium, strontium, barium, aluminium, boron, gallium, indium, tin, lead, antimony, bismuth, scandium, yttrium, lanthanum, titanium, hafnium, 10 vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, thorium, uranium or silicon, whereby preferred mixed metal oxides are cerium 15 with a rare earth or zirconium and/or alumina, zirconium with yttrium, scandium, aluminum or an alkali earth metal, titanium and an alkali or alkali earth metal, manganese, cobalt, nickel and iron in combination with lithium or another alkali metal, lithium and niobium, 20 tungsten or molybdenum, barium with aluminium and platinum, aluminium with platinum or palladium, copper and aluminium or zirconium and zinc, lead and an alkali or earth alkali metal, tin and platinum, indium and tin or zinc, lanthanum and iron, manganese, cobalt or nickel, 25 magnesium and aluminum.

A lot of cheap more or less pure metal chlorides are commercially available. Therefore, it is an advantage of this invention that a mixture of water free 30 metal chlorides can be used as a metals source. Said mixture is then reacted with a carboxylic acid, and thereby formed hydrogen chloride is removed by degassing and/or heating the resulting solution. Such solution then can be used for the manufacture of oxides with a chloride 35 content of less than 0.1% by weight.

The metal oxides of the present invention, in particular the mixed metal oxides, have the applications

already known for them and an extended field of applications due to their improved properties.

Metal oxides of the present invention, such as e.g. ceria, zirconia or ceria/zirconia, due to their
5 great homogeneity can be used for chemomechanical polishing, provided that they are of high purity.

Given the homogeneous particle structure, the oxides of the present invention are furthermore suitable for the manufacture of coatings, in structural ceramics
10 or for protecting layers on metals.

The metal oxides of the present invention are in general e.g. usable as at least part of a catalytically active system, in particular for combustion engines, and/or for chemomechanical polishing, and/or as
15 electrolyte or membranes in solid oxide fuel cells, and/or in batteries or in rechargeable batteries, especially in Li ion batteries, and/or for at least one of the following purposes: as heterogenous catalysts, as NOx storage catalysts, as lubricant, as structural
20 ceramics, as battery storage materials, for chemical sensors, for elements in energy production, for solar energy production elements, for electron storage in recyclable battery units, as dielectrics, as piezoelectrics, in micro-actuators, as ferroelectric, as
25 gas permeable membranes, as pigments, polymer additives, stabilizers; magnetic fluids, polishing powders, additives in metal alloys, in armor fabrication, in microelectronics, as electrode raw material, as phosphors for radiation sensitive elements and in displays, in
30 lasers, cosmetics, pharmaceutical packaging, additive in food and pharmaceutical applications, fuel cells, and/or superconductors.

One preferred use of ceria, and/or preferably ceria/zirconia having a monolithic structure as
35 obtainable according to the present invention is as a catalyst. For such catalyst, the ceria and/or the ceria/zirconia can be mixed with monolithic structure

giving material such as Al_2O_3 . The ceria and/or ceria/zirconia can e.g. be a layer covering a monolithic structure carrier.

Such catalyst may furthermore comprise
5 additional catalytically active substances such as further metal oxides, e.g. titania, vanadia, chromia, manganese, iron, cobalt, nickel, copper oxides, and/or noble metals, e.g. platinum, palladium, rhodium, ruthenium, rhenium, iridium, all of them alone or in
10 admixture with one or more thereof, or alloys thereof. A preferred catalyst is platinum/ceria/zirconia.

Examples *

General Procedure

5 Mixed oxide powders were produced by flame
spray pyrolysis in a laboratory scale setup [Mädler et
al. (2002A), Figure 1] or a pilot-scale oil-burner
(SYSTHERM, CH-8105 Regensdorf, Typ NS1, Ausführung 1.1,
1988, Nr. 20940 ;Control unit (Satronic Type ZT801 and
10 MMD 870; Flicker detector (Satronic IRP 1010); Burner
tube length: 0,23 m, diameter: 0,0825 m; 720 l of
air/hour as dispersion gas, 3 liter of liquid per hour,
Figures 1 and 2).§ The following describes a standard
preparation later denoted as (3/3). Metal containing
15 liquids are brought into the flame by a syringe pump
(Inotech IR-232) at 3 ml/min. The flame consists of a
central spray delivery, a premixed, circular support
flame (diameter 6 mm, slit width 150 µm) and a circular
sheet gas delivery (ring of sinter metal, inner diameter
20 11 mm, outer diameter 18 mm, 5 l oxygen/min.). Oxygen
(Pan Gas, 99.8%) was used as a dispersion gas in all
experiments and delivered at 3 l/min. A mixture of
methane (1.5 l/min, Pan Gas, 99%) and oxygen (3.2 l/min)
was fed to the inner slit and formed a premixed flame.
25 All gas flow rates were controlled by calibrated mass
flow controller (Bronkhorst EL-Flow F201).

Preparation of metal containing precursors

30 Corresponding amounts of metal soaps are
dissolve in xylene, toluene, petroleum, light paraffin
oil or other suitable solvents. Optionally, some
carboxylic acid is added. The following gives a series of
35 preparations with specific substances.

Production of iron or manganese oxide nanoparticles

Iron oxide. 10 ml of iron naphthenate (Strem
5 Chemicals, CAS no. [1338-14-3], LOT no. 138222-S, 80% in
mineral spirits, 12 wt% iron) are mixed with 10 ml of
xylene resulting in a dark red solution. Spraying this
precursor at 3 ml/min (same experimental parameters as in
the ceria/zirconia experiments) in a methane/oxygen spray
10 flame results iron oxide nanoparticles with a BET
specific surface area of 71 m²/g. Production rate: 85 g
iron oxide/liter precursor liquid.

Manganese oxide. 10 ml of manganese
15 naphthenate (Strem Chemicals, CAS no. [1336-93-2], LOT
no. 124623-S, 56% in mineral spirits, 6.0 wt% Mn) are
mixed with 10 ml of xylene and flame sprayed at the same
conditions as for the iron oxide. The corresponding
specific surface area yields 80 m²/g and X-ray
20 diffraction confirms the formation of Mn₃O₄ as a major
component. Production rate: 42 g manganese oxide/liter
precursor liquid.

25 ***Lithium manganese spinell.*** A solution of 0.75
M manganese naphthenate and 0.375 M lithium octoate is
sprayed at (3/3) in a oxygen/methane flame. The product
is kept at 400 °C, in air for 1 h. XRD confirms the
formation of the spinell phase with a specific surface
30 area of 91 m²/g. Narrow particle size distribution is
confirmed by TEM (see Figure 9).

Calcium titanate. 20 ml of a 1.24 M Ca
35 octoate solution (in white spirit/2-ethylhexanoic acid)
and 7.4 ml of titanium tetra isopropoxide are mixed. The
solution warms up as the isopropanol is replaced by the

stronger acid group. The solution is then diluted by two volumes of xylene and sprayed at (3/3) resulting a white powder. XRD confirms formation of calcium titanate (see Figure 8) with a specific surface area of 60 m²/g.

5 Calcination at 600°C, 1h, air results in 45 m²/g.

Barium titanate. 10 ml of a 0.5 M barium octoate solution (2-ethylhexanoic acid/toluene) and 1.51
10 ml of titanium are mixed. After cooling down, 5 ml of toluene are added to reduce the viscosity. Spraying at (3/3) results a pure white powder. Raw material is rather amorphous, but keeping it at 600 °C, 1h in air results a pure barium titanate phase (XRD) with specific surface
15 area of 36 m²/g.

Production of calcia stabilized zirconia

Laboratory scale. 3.5 ml of zirconium (IV) octoate (technical grade, SocTech SA, Bucharest, Rumania, CAS no. [18312-04-4], 16 wt% zirconium), 8.5 ml of 2-ethylhexanoic acid, 5.5 ml of toluene and 0.5 ml of calcium octoate (technical grade, SocTech SA, Bucharest,
25 Rumania, CAS nr [242-197-8], 5.2 wt% calcium) are mixed and sprayed using the standard parameters. The as-prepared powder has a specific surface area of 62 m²/g, sintering in air (16 h at 700 °C, ramp at 5 °C/min) reduces it to 19 m²/g.

30

Pilot scale (first, not optimized trial).

Spraying a mixture of 2 kg zirconium (IV) octoate (technical grade, SocTech SA, Bucharest, Rumania, CAS no. [18312-04-4], 16 wt% zirconium), 0.66 liter light
35 paraffin oil and 0.225 liter of calcium octoate (technical grade, SocTech SA, Bucharest, Rumania, CAS no. [242-197-8], 5.2 wt% calcium) at 3 kg/h in a larger

burner (see General Procedure) results a white, homogeneous powder with 24.5 m²/g. Production rate: 180 g/liter precursor.

5

Production of ceria and ceria/zirconia

Laboratory scale. For ceria, 10.5 ml of cerium (III) octoate (SocTech SA, Bucharest, Rumania, technical grade, CAS no. [56797-01-4], 10,2 wt% cerium, contains 0.14 wt% Na) are diluted with 5.5 ml toluene and 2 ml 2-ethylhexanoic acid. Spraying using the standard parameters results in 67 m²/g and 10 m²/g after sintering in air (16 h at 700 °C, ramp at 5 °C/min). Spraying high grade precursors results in much higher stability as discussed in the Results part.

Pilot scale (first, not optimized trial). Spraying a mixture of 0.75 kg cerium (III) octoate (SocTech SA, Bucharest, Rumania, technical grade, CAS nr [56797-01-4], 10,2 wt% cerium, contains 0.14 wt% Na) and 0.275 liter light paraffin oil at 3 kg/h in a larger burner (see General Procedure) results a slightly yellowish, homogeneous powder with 18 m²/g after sintering in air (16 h at 700 °C, ramp at 5 °C/min) 4 m²/g. Production rate: 90 g/liter precursor.

Laboratory scale. For ceria/zirconia 10.5 ml of cerium (III) octoate (SocTech SA, Bucharest, Rumania, technical grade, CAS no. [56797-01-4], 10,2 wt% cerium, contains 0.14 wt% Na) and 3.5 ml of zirconium (IV) octoate (SocTech SA, Bucharest, Rumania, CAS no. [18312-04-4], 16 wt% zirconium) are diluted with 4 ml toluene. Spraying using the standard parameters results in 69 m²/g and 28 m²/g after sintering in air (16 h at 700 °C, ramp at 5 °C/min). Even using this technical quality

precursors, the effect of stabilization is clearly visible.

Pilot scale (first, not optimized trial).

5 Spraying a mixture of 2.5 kg of cerium (III) octoate
(SocTech SA, Bucharest, Rumania, technical grade, CAS no.
[56797-01-4], 10,2 wt% cerium, contains 0.14 wt% Na),
0.833 kg zirconium (IV) octoate (SocTech SA, Bucharest,
Rumania, CAS no. [18312-04-4], 16 wt% zirconium) and
10 0.833 l toluene at 3 kg/h in a larger burner (see General
Procedure) results a slightly yellowish, homogeneous
powder with 21 m²/g after sintering in air (16 h at 700
°C, ramp at 5 °C/min) 14 m²/g. Production rate: 125
g/liter precursor.

15

Results and Discussion

The importance of viscosity

20 As the metal carrier liquid is dispersed into
small droplets during spraying, viscosity has to be
sufficiently low as to allow good liquid distribution.
The following Table 1 illustrates in what range the
liquid viscosity is appropriate for flame spray
25 synthesis.

Table 1:

Metal carrier liquid	Viscosity /mPa s	Suitable for flame spray if at 298 K
Iron naphthanate 80 % in white spirit	>100	no
Ditto, diluted with xylene (1:1)	3	yes
Manganese naphthenate 56% in white spirit	16	yes
Ditto, diluted with xylene (1:1)	1.7	yes
0.4 M cerium, 0.4 M zirconium in 2-Ethylhexanoic acid/Toluene (5:2 by volume)	5	yes
Zirconium octoate (16 wt% Zr) in white spirit	>100	no
Ditto, diluted with xylene (3:1)	10	yes
Ditto, diluted with dodecane (3:1)	19	yes
Cerium octoate (10.2 wt% cerium) in white spirit, diluted with xylene (3:1)	22	yes
Ditto, diluted with dodecane (3:1)	>40	dependent on burner

Note: Viscosity measured in a rheometer (Haake VT 550
 5 Rheometer, Fisons, Digitana AG, 8810 Horgen) at ambient temperature

Diluting metal carboxylates with other
 solvents shows the colligative properties of these
 10 solutions. Xylene reduces the viscosity about twice as
 good as dodecane for both cerium and zirconium
 precursors.

As an alternative to dissolution, or in
 addition thereto, heating of the metal carboxylate or the
 15 metal carboxylate comprising mixture/solution can be
 provided, in order to further lower the viscosity to
 preferably beyond 40 mPa s.

The importance of material purity on thermal stability

As additional elements, sodium or chloride form the manufacturing process of the carboxylate salts of metals, have a significant influence on the final product stability, a comparison is given form precursors of high purity (>99% metal content) and technical grades (below 99% metal, contains chloride and mainly sodium). A large drop in stability after sintering becomes most apparent for ceria where sodium in the technical precursor increases its sintering rate. A cross experiment with pure cerium octoate and an additional 1 wt% sodium resulted in a similar loss in specific surface area as in the case of the technical grade precursors. The results are shown in Table 2 below.

Table 2:

	grade	SSA as prepared [m ² g ⁻¹]	SSA sintered [m ² g ⁻¹]	Prod. Rate [g l ⁻¹]
	99.8%	125	71	69
	Tech.	67	10	69
Ceria, 1 wt% Na		-	24 ^a	-
Zirconia	>99%	105	45	50
"	Tech.	121	24	50
Ceria/zirconia	>99%	94	83	59
"	Tech.	69	28	59

Note: Technical grades contain sodium and chloride amongst others.

^a Pure, flame made ceria is impregnated with sodium hydroxide (1 wt% Na₂O in final ceramic) and subjected to sintering.

25

grade: purity based on metals only

The range of accessible materials

The given examples show that single
5 transition metal oxides can be prepared with above 60
m²/g specific surface area while maintaining production
rates of more than 40 g/h. Such materials find
applications in a wide range of products and processes.
Electronic materials, batteries, ferroelectrics,
10 permanent magnets, coils, and magnetic fluids are just a
few.

The given examples further show that an
alkaline or earth alkaline metal can be combined with a
transition metal oxide to form the corresponding mixed
15 oxides. Such materials can form spinells, perovskites and
other interesting phases. They find applications as
dielectric, piezoelectrics, actuators, in membranes, as
sensors, in capacitors, superconductors and others. Some
are used as catalysts, as ceramics for high temperature
20 applications or structural ceramics.

Material homogeneity

25 Transmission electron microscopy images of
lithium manganate, calcium titanate or ceria/zirconia
show that nanoparticle with a narrow range of particle
sizes can be obtained by the here described method. This
is further supported by X-ray diffraction pattern that
30 would show the formation of large crystallites. Specific
surface area, furthermore supports the particle size
range as observed by TEM. This data clearly show that the
present invention can be used for the manufacture of
nanoparticles.

Conclusions

The carboxy process offers a readily accessible way to nanoparticle production. Using metal
5 soaps as main precursors even conventional oil burners may be used to synthesize nanoparticles. Particles of transition metal oxides, mixed oxides from elements from the alkali metal, alkaline earth metal, rare earth metal and transition metal series amongst them have been made
10 showing the versatility of the process. Handling, storage and mixing compatibility of such metal soap based liquids are combined with high production rate. Enabling over 200 g of nanoparticles to be produced from 1 liter of precursor liquids while being rather insensitive to the
15 type of burner, dispersion gas system or flame type makes these precursors very advantageous over any other metal delivery system for flame spray synthesis.

Even technical precursors may be used but consequently result in much lower thermal stability. A
20 proof of this effect was made by doping sodium into a pure ceria precursor (see Table 2).

While there are shown and described presently
25 preferred embodiments of the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practiced within the scope of the following claims.

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Claims

1. A method for the production of a metal oxide wherein at least one metal precursor that is a metal carboxylate with a mean carbon value per carboxylate group of at least 3 is formed into droplets and oxidized in a high temperature environment.

2. The method of claim 1 wherein the mean carbon value per carboxylate group is at least 4, preferably at least 5, most preferred between 5 and 8.

3. The method of claim 1 or 2 wherein the metal carboxylate is oxidized in a flame.

4. The method of anyone of the preceding claims wherein the metal carboxylate prior to being formed into droplets has a viscosity of at most 100 mPa s, preferably at most 40 mPa s, more preferably at most 20 mPa s.

5. The method of claim 4, wherein the viscosity is obtained by heating and/or by providing a mix of the at least one metal carboxylate and at least one viscosity reducing solvent.

6. The method of claim 3 wherein the viscosity reducing solvent comprises at most 40 % w/w of acid(s).

7. The method of claim 6 wherein the solvent comprises no acid.

8. The method of anyone of claims 5 to 7, wherein the solvent comprises at least one low molecular weight and/or low viscosity apolar solvent, in particular an aromatic or aliphatic, unsubstituted, linear or branched hydrocarbon, preferably a solvent selected from the group consisting of toluene, xylene, lower aliphatic hydrocarbons and mixtures thereof.

9. The method of anyone of the preceding claims, wherein the metal carboxylate is selected from the group consisting of C1 to C18 carboxylates and mixtures thereof, preferably C4 to C12 carboxylates and

mixtures thereof, much preferably C5 to C8 carboxylates and mixtures thereof, in particular octoates such as 2-ethylhexanoic acid salts.

10. The method of anyone of the preceding
5 claims, wherein the metal or the combination of metals is selected from cerium, zirconium, any rare earth metal, lithium, sodium, potassium, rubidium or caesium, magnesium, calcium, strontium, barium, aluminium, boron, gallium, indium, tin, lead, antimony, bismuth, scandium,
10 yttrium, lanthanum, titanium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, thorium, uranium and silicon,
15 whereby preferred mixed metal oxides are cerium with a rare earth or zirconium and/or alumina, zirconium with yttrium, scandium, aluminum or an alkali earth metal, titanium and an alkali or alkali earth metal, manganese, cobalt, nickel and iron in combination with lithium or
20 another alkali metal, lithium and niobium, tungsten or molybdenum, barium with aluminium and platinum, aluminium with platinum or palladium, copper and aluminium or zirconium and zinc, lead and an alkali or earth alkali metal, tin and platinum, indium and tin or zinc,
25 lanthanum and iron, manganese, cobalt or nickel, magnesium and aluminum.

11. The method of anyone of the preceding claims wherein the flame oxidation is performed in a spray burner, or in particular in an oil burner.

30 12. The method of anyone of the preceding claims wherein the oxidation is performed at a temperature of at least 600°C, preferably at least 800°C, more preferably at least 1000°C and most preferably in a range of 1200 to 2600°C, in particular at about 1600 °C.

35 13. The method of anyone of the preceding claims wherein the metal carboxylate is prepared starting from a metal oxide, a metal hydroxide, a metal carbonate,

a metal halide, such as a chloride or bromide, or a metal lower alkyl oxide, in particular a C1 to C4 alkyl oxide.

14. The method of anyone of the preceding claims, wherein the enthalpy of the metal carboxylate or the metal carboxylate comprising solution is at least 13 kJ/g, preferably at least 18 kJ/g, more preferred at least 22.5 kJ/g and most preferred at least 25.5 kJ/g.

15. The method of anyone of the preceding claims, wherein the metal carboxylates comprise impurities of one or more elements of the group comprising alkali metals, alkaline earth metals, transition metals, rare earth metals, chlorides, fluorides, bromides, phosphates, sulfates, silicon, and main group metals such as Al, B etc., whereby the impurities are present in amounts in the range of 0.5 to 5 % by weight, in particular from 0.8 to 5 % by weight.

16. The method of anyone of the preceding claims, wherein the solution comprises at least 0.15 moles metal per liter, leading to production rates of at least 0.15 moles metal or metal oxide per nozzle.

17. The method of anyone of the preceding claims wherein the metal oxide is produced in a flame with insufficient oxygen for full conversion resulting in the formation of substoichiometric oxides or metals and mixtures thereof.

18. The method of anyone of the preceding claims where the as produced metal oxide is converted to the corresponding non-oxides such as nitrides, borides, carbides by means of an additional treatment.

19. A method for the production of metal carboxylates wherein one or more water free metal chlorides are used as a metals source, said metals source is reacted with a carboxylic acid such that hydrogen chloride is generated which is removed, in particular by degassing and/or heating the resulting solution, whereby a solution is obtained that is suitable for the manufacture of oxides with a chloride content of less

than 0.1% by weight, in particular by a method of one of the preceding claims.

20. Pure transition metal oxides and mixed alkali or alkaline earth metal and transition metal
5 oxides such as alkali metal manganates, especially lithium manganate or cobaltates, or such as calcium, strontium, barium titanates or zirconates and mixtures thereof, and iron or manganese oxide having a high thermal stability that is characterized by a specific
10 surface area (BET) of at least 20 m²/g after sintering at 1 h at 600 °C, and preferably obtainable with a method of anyone of claims 1 to 18.

21. Pure or mixed metal oxides with impurities such as alkali metals, alkaline earth metals, transition
15 metals or rare earth metals, but also chlorides, fluorides or bromides, phosphates, sulfates or silicon in the range of 0.5 to 5 % by weight, in particular from 0.8 to 5 % by weight, that have a specific surface area (BET) of at least 5 m²/g, preferably at least 10 m²/g, more
20 preferably at least 15 m²/g, and that are preferably obtainable by the method of anyone of claims 1 to 18.

22. A metal oxide, in particular a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 21 that has a
25 geometric standard deviation of the mass averaged primary particle size distribution of smaller than 2 or less than 2 wt% of solid primary particles with more than 500 nm in diameter, and a specific surface area of more than 3 m²/g.

30 23. Use of a metal oxide of claim 19 as in powder injection molding or in optical lens polishing.

24. A metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 22, that is zirconia stabilized with cerium and/or
35 yttrium, preferably cerium or yttrium, in particular in an amount of cerium and/or yttrium of at most 20 %

25. Use of a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 as at least part of a catalytically active system, in particular for combustion engines.

5 26. The use of claim 25, wherein the catalytic applications are the manufacture of car exhaust catalysts, and wherein the oxides preferably are ceria based oxides, optionally with platinum group metals.

10 27. Use of a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 for chemomechanical polishing, provided that the metal oxide is of high purity, in particular 99 % pure by weight.

15 28. Use of a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 as electrolyte or membranes in solid oxide fuel cells.

20 29. Use of a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 in batteries or in rechargeable batteries, especially in Li ion batteries.

30 30. Use of a metal oxide obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 for at least one of the following purposes: as heterogenous catalysts, as NOx storage catalysts, as lubricant, as structural ceramics, as battery storage materials, for chemical sensors, for elements in energy production, for solar energy production elements, for electron storage in recyclable battery units, as dielectrics, as piezoelectrics, in micro-actuators, as ferroelectric, as gas permeable membranes, as pigments, polymer additives, stabilizers, magnetic fluids, polishing powders, additives in metal alloys, in armor fabrication, in microelectronics, as electrode raw material, as phosphors for radiation sensitive elements and in displays, in lasers, cosmetics, pharmaceutical packaging, additive in food and

35

pharmaceutical applications, fuel cells, and/or superconductors.

31. A catalyst comprising ceria, and/or preferably ceria/zirconia obtainable by the method of anyone of claims 1 to 18 or according to anyone of claims 20 to 23 and having a monolithic structure.

32. The catalyst of claim 31 comprising the ceria and/or the ceria/zirconia mixed with monolithic structure giving material such as Al_2O_3 .

33. The catalyst of claim 31 or 32 comprising ceria and/or ceria/zirconia in a layer covering a monolithic structure carrier.

34. The catalyst of anyone of claims 31 to 33 comprising additional catalytically active substances such as further metal oxides, e.g. titania, vanadia, chromia, manganese, iron, cobalt, nickel, copper oxides, and/or noble metals, e.g. platinum, palladium, rhodium, ruthenium, rhenium, iridium, all of them alone or in admixture with one or more thereof, or alloys thereof.

1/7

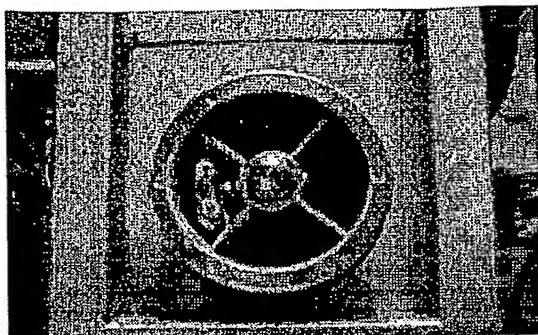


Figure 1



Figure 2

2/7

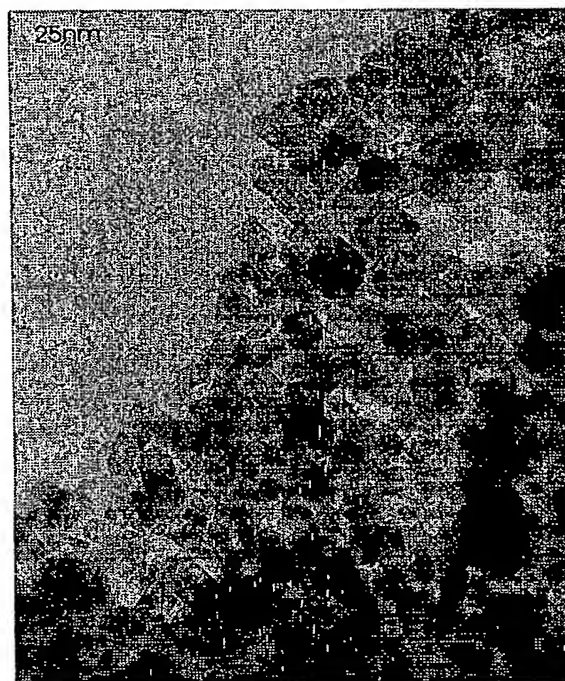
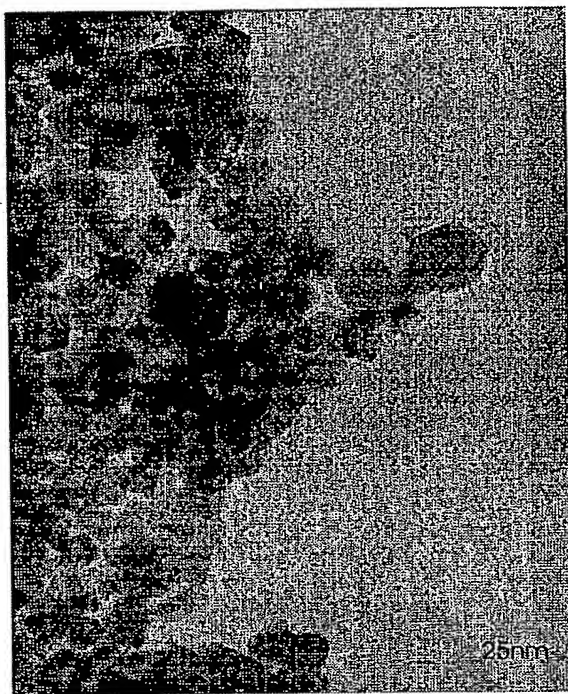


Figure 3

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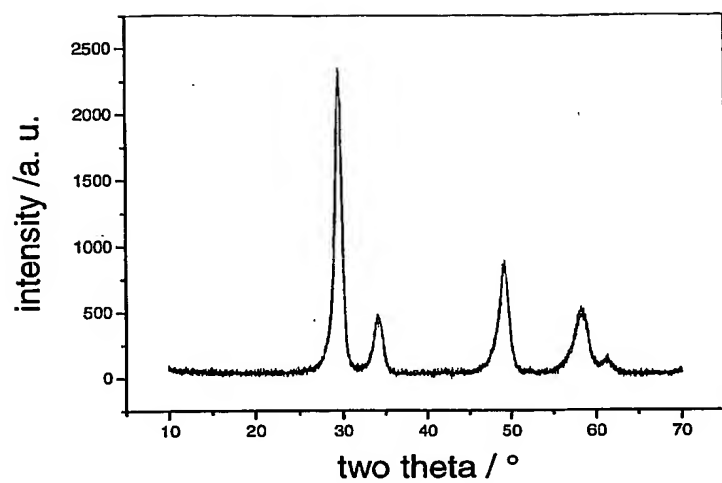


Figure 4

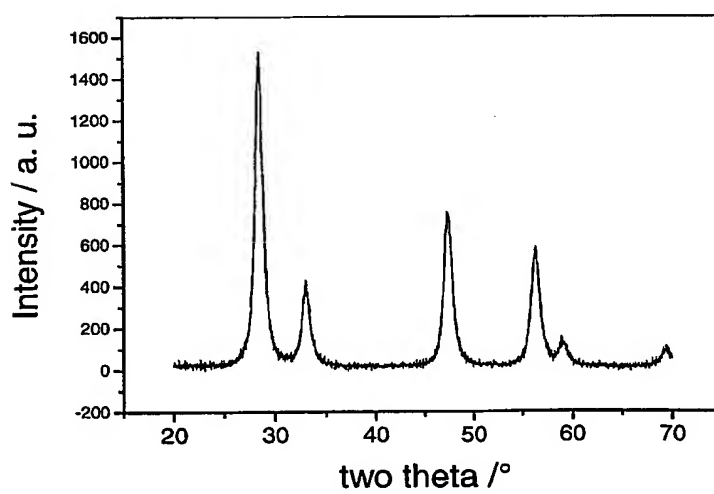


Figure 5

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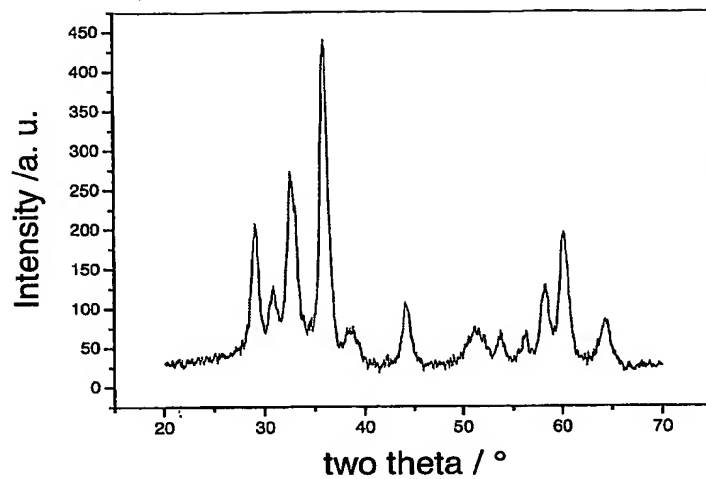


Figure 6

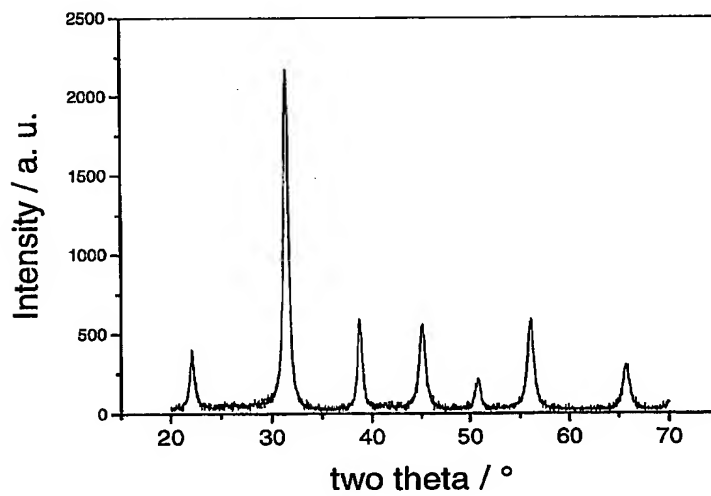


Figure 7

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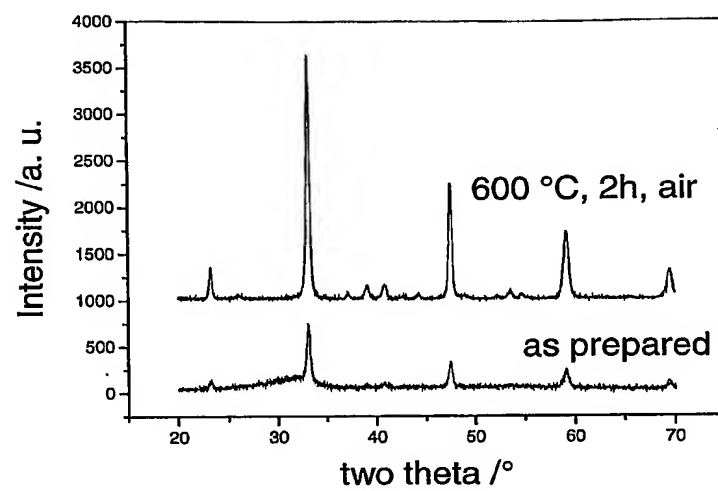


Figure 8

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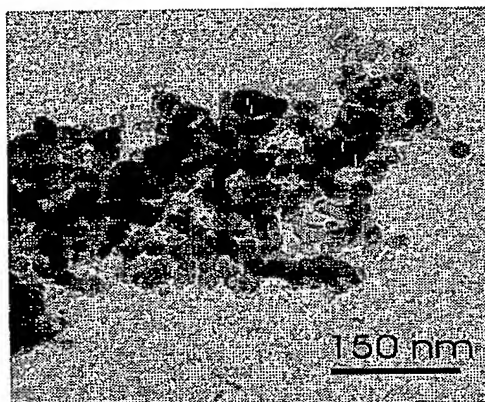
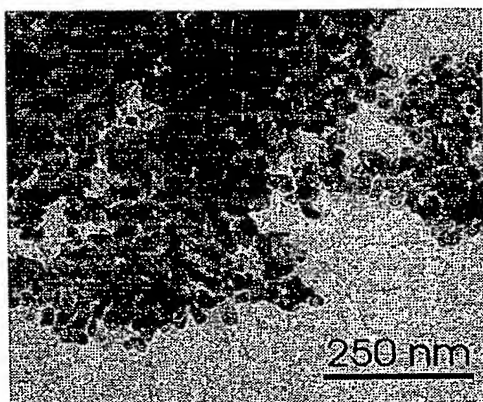


Figure 9

7/7

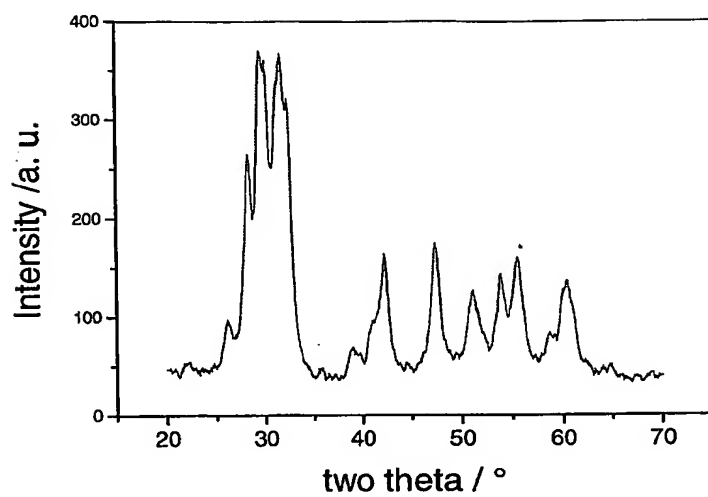


Figure 10

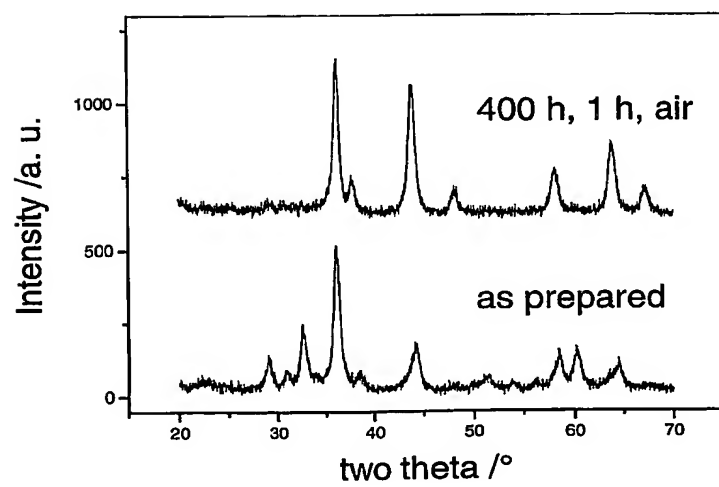


Figure 11